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Effect of Chloride Concentration, pH, and Scan Rate on Pitting Corrosion of Fe-Ni-Cr-Mo Alloys

Ajit K. Roy
Dennis L. Fleming
Steven R. Gordon

The results of a recent electrochemical study performed on several candidate waste package container materials at the Lawrence Livermore National Laboratory (LLNL) indicate that iron-nickel-chromium-molybdenum (Fe-Ni-Cr-Mo) Alloys 825, G-3, and G-30 may suffer from pitting corrosion in an acidic brine containing 5 weight percent (wt%) NaCl at 90°C under potentiodynamic and potentiostatic controls. In an effort to study the effect of chloride ion (Cl^-) concentration, pH, and electrochemical potential scan rate on the susceptibility of these materials to pitting corrosion, additional cyclic potentiodynamic polarization tests have been performed in neutral, acidic, and alkaline salt solutions containing 1, 5, and 10 wt% NaCl at 90°C. The pH of these solutions ranged between 6 and 7, 2 and 3, and 10 and 11, respectively. Dynamic potential scans were carried out in the noble direction at rates of 0.043, 0.085, 0.17, and 0.34 mV/sec commencing at the stable corrosion potential, and continuing to a potential sufficiently noble to cause pitting prior to reversing the scan at the same rate. Consistent with results of other investigators, the present study showed a shift in the critical pitting potential (E_{pit}) to more active values with increasing Cl^- concentration. As to the effect of pH, E_{pit} was significantly shifted to more noble values with a change in pH from acidic to neutral, as expected. At alkaline pH, Alloys G-3 and G-30 showed slightly lower E_{pit} values compared to those in neutral solution. However, E_{pit} for Alloy 825 was shifted to more noble values at alkaline pH. No consistent pattern in the effect of Cl^- concentration and pH on the protection potential was observed. With respect to the effect of potential scan rate on E_{pit} , a general trend was not observed. In some cases, increasing the scan rate caused E_{pit} to become more noble. In other cases, the opposite behavior occurred.

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Ajit K. Roy
Framatome Cogema Fuels, Livermore, CA
and
Dennis L. Fleming
Steven R. Gordon
Lawrence Livermore National Laboratory, Livermore, CA

Results

Electrochemical potentiodynamic and potentiostatic polarization experiments were performed at the Lawrence Livermore National Laboratory (LLNL) on several candidate waste package container materials to evaluate their susceptibility to pitting corrosion in neutral, acidic, and alkaline brines containing 5 weight percent (wt%) NaCl at ambient temperature, 60°C, and 90°C. Results[1-3] indicate that iron-nickel-chromium-molybdenum (Fe-Ni-Cr-Mo) Alloys 825, G-3, and G-30 may suffer from pitting corrosion in the acidic brine at 90°C. However, Ni-base Alloys C-4 and C-22, and titanium-base alloy Ti Gr-12 were immune to pitting corrosion in all tested environments.

In an effort to study the effect of chloride ion (Cl^-) concentration, pH, and electrochemical potential scan rate on the susceptibility of these alloys to pitting corrosion, additional cyclic potentiodynamic polarization (CPP) tests were recently conducted at LLNL in neutral, acidic, and alkaline brines containing 1, 5, and 10 wt% NaCl at 90°C. The pH of these solutions ranged between 6 and 7, 2 and 3, and 10 and 11, respectively. Dynamic potential scans were carried out in CPP experiments in the noble direction at rates of 0.043, 0.085, 0.17, and 0.34 mV/sec commencing at the stable corrosion potential (E_{corr}), and continuing to a potential sufficiently noble to cause pitting prior to reversing the scan rate at the same rate.

In electrochemical terms, the initiation of pitting occurs at a critical potential[4], E_{pit}, at which the anodic polarization curve changes its slope abruptly, showing a dramatic increase in current density. For susceptible alloys, a hysteresis is observed as the direction of potential scan is reversed after some degree of polarization above E_{pit}. The crossover at the passive current density defines a repassivation or protection potential, E_{prot}, below which established pits are presumed not to continue to grow. By contrast, new pits can initiate only at potentials above E_{pit}. Between E_{prot} and E_{pit}, new pits cannot initiate, but old ones can still grow.

Results indicate that Alloys 825, G-3, and G-30 underwent pitting corrosion at all three chloride concentration levels tested. Figure 1 shows a plot of E_{pit} as a function of Cl^- concentration for all three alloys in acidic brines, showing a shift in E_{pit} to more negative (or active) values with increasing Cl^- concentration. The extent of pitting in Alloy G-30 was significantly less than that observed for Alloys 825 and G-3. Alloys C-4, C-22, and Ti Gr-12 did not exhibit any pitting tendency under any environmental conditions.

The relationship between E_{pit} and pH for susceptible alloys in solutions containing 10 wt% NaCl is shown in Figure 2. For all three materials, E_{pit} was significantly shifted to more noble values with a change in pH from acidic to neutral, as expected. At alkaline pH, Alloys G-3 and G-30 showed slightly lower E_{pit} values compared to those in neutral solution. However, E_{pit} for Alloy 825 was shifted to a more positive value at alkaline pH.

As to the effect of potential scan rate on E_{pit} , a general trend has not yet been observed. At the time of this writing, tests are still being continued to evaluate the effect of this parameter on E_{pit}. Based on the data available so far, in some cases, increasing the scan rate caused E_{pit} to become more noble. In other cases, the opposite behavior occurred.

Acknowledgments

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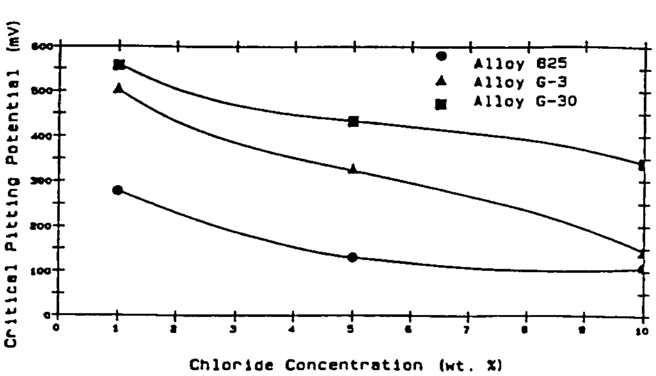

Figure 1. Critical Pitting Potential (E_{pit}) vs Chloride Concentration in Acidic Solutions (pH~2.36 - 2.85) at 90°C

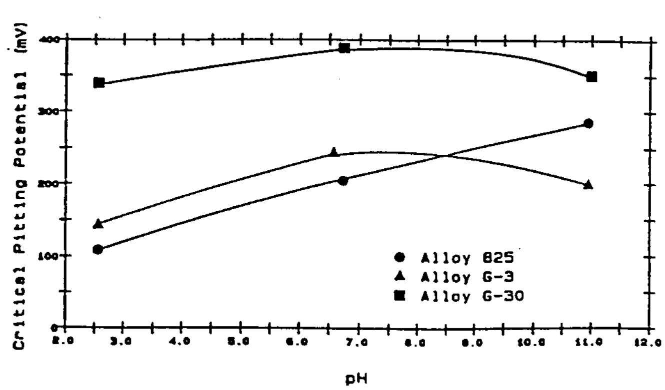

Figure 2. Critical Pitting Potential (E_{pit}) vs pH in Aqueous Solutions Containing 10 wt% NaCl at 90°C